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Thermodynamic Properties of Hedenbergite, a Complex Silicate of Ca, Fe, Mn, and Mg

By K. O. Bennington, R. P. Beyer, and R. R. Brown



UNITED STATES DEPARTMENT OF THE INTERIOR

Report of Investigations 8873

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UNIT OF MEASURE ABBREVIATIONS USED IN THIS REPORT

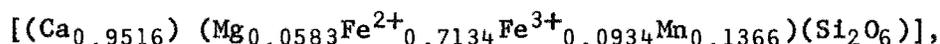
°C	degree Celsius	kcal/mol	kilocalorie per mol
cal	thermochemical calorie	K/min	degree kelvin per minute
cal/mol·K	calorie per mol per degree kelvin	mL	milliliter
cm	centimeter	μm	micrometer
g	gram	pct	percent
J	joule	ppm	part per million
K	kelvin	wt pct	weight percent
kcal	kilocalorie		

THERMODYNAMIC PROPERTIES OF HEDENBERGITE, A COMPLEX SILICATE OF Ca, Fe, Mn, AND Mg

By K. O. Bennington,¹ R. P. Beyer,² and R. R. Brown¹

ABSTRACT

The thermodynamic properties of hedenbergite, of composition



were experimentally determined at the Bureau of Mines. The standard enthalpy of formation determined by hydrofluoric acid solution calorimetry is

$$\Delta H_{298}^{\circ} = -680.96 \pm 0.855 \text{ kcal/mol.}$$

The standard enthalpy of formation from the oxides is

$$\Delta H_{298}^{\circ} = -24.55 \pm 0.485 \text{ kcal/mol.}$$

Low-temperature heat capacities were determined by adiabatic calorimetry from 12.3 to 300.1 K. The derived standard entropy is

$$S_{298}^{\circ} = 41.218 \pm 0.148 \text{ cal/mol}\cdot\text{K.}$$

High-temperature heat capacities were measured with a differential scanning calorimeter from 397 to 1,147 K.

These experimentally determined data were combined with data from the literature to calculate the Gibbs energies of formation and equilibrium constants of formation over the temperature range of measurements. Standard enthalpies of formation are given as a function of temperature. The standard Gibbs energy of formation at 298.15 K is

$$\Delta G_{298}^{\circ} = -641.90 \pm 0.86 \text{ kcal/mol.}$$

INTRODUCTION

This investigation of the thermodynamic properties of hedenbergite is one of a series being performed at the Bureau of Mines on slag-type pyroxenes, which include

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the pair acmite $[(\text{NaFe}^{3+})(\text{Si}_2\text{O}_6)]$ and the nearly identical mineral aegirine. These pyroxene minerals readily assimilate manganese; consequently, this study contributes toward both the future investigation of some manganese minerals and the understanding of slag action in steelmaking.

MATERIALS

Acids

The acids were reagent-grade products that were used without treatment except for dilution with distilled water to the proper strength.

Silica

The silica (SiO_2) used was from an exceedingly clear and pure, single, natural, quartz crystal. The crystal was sawed, crushed, ground to pass a 400-mesh screen, and elutriated in distilled water. The size fraction ranging between 10 and 20 μm was retained for the heat of solution measurements. This fraction was repeatedly leached with dilute hydrochloric acid until the solution remained clear; it was then digested with hydrogen peroxide and dried. Each sample was heated through the alpha-beta transition immediately before solution measurements were made. No impurities were detected spectrographically, and the X-ray diffraction pattern matched the pattern listed on the powder diffraction file (9)³ (PDF), card 5-490 for alpha-quartz.

Manganous Oxide

Reagent-grade MnO_2 was slowly heated in a stream of hydrogen until a temperature of 850° C was reached. It was held at this temperature for several hours, then it was blended, sampled, and analyzed, after which the process was repeated. Final X-ray analysis showed the product to be only face-centered cubic manganous oxide (MnO), and the pattern matched that given on PDF card 7-230. No corrections were made for spectrographically detected impurities; the maximum total for Mg and Si is ~100 ppm, and the maximum total for Al, Ca, and Fe ~400 ppm.

Ferric Oxide

The ferric oxide (Fe_2O_3) was a high-purity product that was used without alteration except to dry to constant weight. Only $\alpha\text{-Fe}_2\text{O}_3$ was detected by X-ray analysis, and the pattern matched that given on PDF card 13-534. No corrections were made for the spectrographically detected amounts (~400 ppm) of manganese and silicon.

Ferrous Sulfate Heptahydrate

The ferrous sulfate heptahydrate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$) was a reagent-grade product. On analysis, it was found to have an $\text{Fe}:\text{SO}_4:\text{H}_2\text{O}$ ratio of 1.000:0.993:7.04. There was no detectable trace of ferric iron. Compensation for the slight excess of water was made in the calorimetric correction procedure. Samples were weighed, individually double-sealed, and stored in a desiccator until used.

Calcium Oxide

Reagent-grade CaCO_3 of very high purity was roasted overnight at 970° C to provide the calcium oxide (CaO) for each determination.

³Underlined numbers in parentheses refer to items in the list of references at the end of this report.

Hedenbergite

Analysis

The hedenbergite $[(Ca_{0.9516})(Mg_{0.0583}Fe^{2+}_{0.7134}Fe^{3+}_{0.0934}Mn_{0.1366})(Si_2O_6)]$ used in this study was crystalline material, with crystals commonly 1 to 2 cm across, and a few large clusters 3 to 5 cm across. This material was collected at the Laxey Mine, South Mountain, ID. Some crystals showed evidence of surface alteration, probably weathering. Some particles showing surface alteration remained in spite of very careful selection. Only hedenbergite was detected by X-ray analysis, and the structure pattern matched that given on PDF card 16-701.

The chemical analysis, presented in table 1, was made at the Branch of Analytical Laboratories, U.S. Geological Survey, Menlo Park, CA.

Formula

The formula for hedenbergite and the formula weight were calculated from the chemical analysis using the anion-based hydrogen-equivalent method. This method for deriving the number of ions per mineral formula consists of calculating the ratios of hydrogen equivalents of the analyzed constituents and normalizing these values to the ideal sum of anions per unit formula. A detailed description for the calculations for this technique is given by Jackson (11). This procedure was described earlier by Miser (14) and Stevens (20-21) and more recently by Goff (8).

TABLE 1. - Analysis of hedenbergite¹

Composition		Ions in extended formula	Formula wt, g	Charge ²	Substitution site	Adjusted formula	
Oxides	wt pct					Ions	wt, g
SiO ₂	49.18	2.0042	56.289	8.0170	Fe ₂ O ₃	2.000	56.171
Al ₂ O ₃37	.0178	.480	.0534	Fe ₂ O ₃		
P ₂ O ₅05	.0017	.053	.0086	Fe ₂ O ₃		
Fe ₂ O ₃	2.19	.0672	3.753	.2015		.0934	5.216
FeO.....	20.93	.7134	39.841	1.4265		.7134	39.841
MnO.....	3.96	.1366	7.504	.2733		.1366	7.504
MgO.....	.96	.0583	1.417	.1165		.0583	1.417
CaO.....	21.67	.9462	37.924	1.8923		.9516	38.140
Na ₂ O.....	.13	.0103	.237	.0103	Ca		
K ₂ O.....	.01	.0005	.019	.0005	Ca		
³ H ₂ O ⁺16						
⁴ H ₂ O ⁻46						
O.....		6.000	95.996				95.996
Total.....	100.07	Nap	243.513	Nap	Nap	Nap	244.285

Nap Not applicable.

¹Analyst: Sarah T. Neil, chemist, U.S. Geological Survey, Menlo Park, CA.

²Equivalents per formula.

³Bound water.

⁴Hygroscopic water. Total water calculated out.

It is necessary to make several assumptions in the construction of this formula. Following Jackson (11) and Sommerfeld (19), it is assumed that all of the anion positions in the mineral structure are filled and that the charges in the mineral are balanced. Jackson has pointed out that under these assumptions, cation deficiencies may be due to vacant cation positions or analytical errors, and further, that if the type formula for the mineral is correctly chosen, any calculated excess of cations may be due to only analytical error. For the purposes of this study, the chemical analysis is considered to be absolutely accurate; consequently, information is shown in the necessary detail and completeness for recalculation.

The number of atoms of the individual elements in the extended formula was used in computing the formula weight, the total of which provides the gram formula weight of the natural mineral. The grouping of ions into particular positions follows the example of Deer (6). The numbers of ions, even though unrealistic, were carried without rounding to maintain internal consistency.

The number of ions in the extended formula does not provide a practical composition; consequently, it was adjusted by substituting the impurity elements into the most likely sites. The deviations in each structural position represent the difference between the ideal stoichiometry and the sum of ions substituted per structural site. The positions, as shown under the column marked "Charge" (equivalents per formula) in table 1, are shown to be almost exactly balanced. The equivalents per formula for the excess SiO_2 , and the total charge for the Al_2O_3 and P_2O_5 impurities are added to the ferric iron position, then divided by the valence of ferric iron to provide the total number of ions in this position in the adjusted formula.

The adjusted formula weight for each structural position provides the total adjusted formula weight. The construction necessary to develop the adjusted formula and formula weight requires that corresponding heat corrections be made. The heat of solution corrections for cation substitutions and impurities were made by treating the impurity elements as substituted into the most likely major element sites, as previously described. The energy difference is that calculated between the quantity of the major element that has been displaced by an equal quantity of the proxying element, and was computed from the respective heats of solution values of their oxides, determined under similar conditions. The corrections applied were the net energy differences for the specific number of ions in a particular structure position.

The thermal correction required by the change in gram formula weight was applied by scaling the heat of solution value for the natural mineral to the adjusted gram formula weight. This was done assuming that the vacancy sites are uniformly distributed, that the added ions are completely bonded in the structure, and that the heat of solution of the natural mineral is more suitable than a thermal adjustment based on the separate heats of solution of the deficient or excess oxides.

The values for the thermal corrections and sequence of application of the corrections are given in detail under the reaction description for the mineral, reaction 9, in the hedenbergite reaction scheme, table 2. The heat of solution values were determined and calculated for the formula weight of the natural mineral, and the corrections were then applied.

EXPERIMENTAL DETERMINATIONS

Heats of Solution at 298.15 K

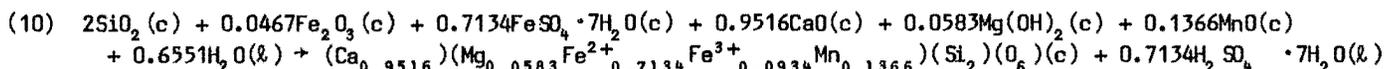
The heat of solution of hedenbergite was determined by hydrofluoric acid solution calorimetry. The apparatus used has been described in earlier publications (1, 12, 24). The solvent used was 948.7 g of 20.1 wt pct hydrofluoric acid to which approximately 0.60 g $K_2Cr_2O_7$ was added. The quantities of all reaction substances were stoichiometric with 0.601 g of alpha-quartz, which, when substituted into reaction 1, table 2, provides the stoichiometric molar proportions of all succeeding reactions.

Weighed amounts of solid or liquid substances to be dissolved were placed in paraffin-sealed Teflon⁴ fluorocarbon polymer tape capsules and dropped at the appropriate time, at 25° C, into the calorimeter, which was operated at 73.7° C. Each measurement resulted from a process of converting the pure reaction substances at 25° C plus the solvent at 73.7° C to a solution product at 73.7° C. Corrections were applied for the heat effects of the paraffin, Teflon, and a gold ballast, when used. Electrical calibrations of the calorimeter were made over the temperature range of measurements.

TABLE 2. - Reaction scheme for hedenbergite¹

Reaction	ΔH	
	kcal	Uncertainty, \pm kcal
(1) $2SiO_2(c) + 12HF(sol) \rightarrow 2H_2SiF_6(sol) + 4H_2O(sol)$	-65.818	0.010
(2) $0.6551H_2O(l) \rightarrow 0.6551H_2O(sol)$538	.001
(3) $0.1366MnO(c) + 0.2732H^+(sol) \rightarrow 0.1366Mn^{2+}(sol) + 0.1366H_2O(sol)$	-6.442	.002
(4) $0.0467Fe_2O_3(c) + 0.2802H^+(sol) \rightarrow 0.0934Fe^{3+}(sol) + 0.1401H_2O(sol)$	-1.963	.002
² (5) $0.7134FeSO_4 \cdot 7H_2O(c) \rightarrow 0.7134Fe^{3+}(sol) + 0.7134SO_4^{2-}(sol) + 4.9938H_2O(sol)$...	-14.732	.018
(6) $0.9516CaO(c) + 1.9032HF(sol) \rightarrow 0.9516CaF_2(p) + 0.9516H_2O(sol)$	-52.934	.019
(7) $0.0583Mg(OH)_2(c) + 0.1166HF(sol) \rightarrow 0.0583MgF_2(p) + 0.1166H_2O(sol)$	-1.077	.007
(8) $0.7134H_2SO_4 \cdot 7H_2O(l) \rightarrow 1.4268H^+(sol) + 0.7134SO_4^{2-}(sol) + 4.9938H_2O(sol)$	4.584	.016
² (9) $(Ca_{0.9516})(Mg_{0.0583}Fe^{2+}_{0.7134}Fe^{3+}_{0.0934}Mn_{0.1366})(Si_2O_6)(c)$ + $14.0198HF(sol) + 1.9802H^+(sol) \rightarrow 0.9516CaF_2(p) + 0.0583MgF_2(p)$ + $0.8068Fe^{3+}(sol) + 0.1366Mn^{2+}(sol) + 2H_2SiF_6(sol) + 6H_2O(sol)$ ³	-148.74	.400

$$\Delta H_{10} = \Delta H_1 + \Delta H_2 + \Delta H_3 + \Delta H_4 + \Delta H_5 + \Delta H_6 + \Delta H_7 - \Delta H_8 - \Delta H_9$$



$$\Delta H_{10} = 1.728 \pm 0.401 \text{ kcal}$$

¹For reactions 1-9 introduced reactants are at 25° C and reaction products are at 73.7° C.

²Ferrous iron is oxidized in solution to ferric, which is equally balanced and cancelled in reaction 9.

³Corrected value.

NOTE.--Symbols c, l, g, sol, and p in parentheses denote substances that are crystalline, liquid, gas, in solution, or crystalline precipitate, respectively, in all reactions.

⁴Reference to specific brand names or manufacturers is made for identification only and does not imply endorsement by the Bureau of Mines.

Throughout this report, uncertainties were assigned to measured and derived heat values as follows: (1) When several individual heat values were measured for a reaction, the precision uncertainty was taken as $2\sqrt{\sum d_i^2/n(n-1)}$, where $\sum d_i^2$ is the sum of the squares of the deviations from the mean value and n is the number of determinations; (2) when the heats of two or more reactions were added, the uncertainty was taken as the square root of the sum of the squares of the uncertainties for the individual reactions. These procedures followed the recommendations of Rossini and Deming (18).

All energy units are expressed in terms of the defined thermochemical calorie (1 cal = 4.1840 J). All weighings were corrected to vacuum, and molecular weights are in accordance with the 1979 table of atomic weights (10). Final values are rounded to 10 cal. All calibrations are traceable to the National Bureau of Standards (NBS), and sample temperatures are based on the International Practical Temperature Scale of 1968 (IPTS-68) (5).

The reaction scheme for the solution calorimetric investigation is given in table 2. The symbols c, l, g, sol, and p in parentheses are used to denote substances that are crystalline, liquid, gas, in solution, or crystalline precipitate, respectively. The reactions are written in an abbreviated form sufficient to show that stoichiometry was maintained to permit cancellation of the reaction products. The table also contains the mean measured heat values and their precision uncertainties.

The experimentally determined heat of solution data together with the mean values and the precision uncertainties are listed in table 3. The data for reaction 7, the dissolution of $Mg(OH)_2$ (brucite), was previously determined (2) under nearly identical conditions, and the mean value of -18.479 ± 0.12 kcal/mol was adopted directly.

Reaction 9 represents the heat of solution of the mineral hedenbergite in the solution following reaction 8. The mean value of seven determinations is -147.595 ± 0.205 kcal as shown in table 3. This value is for the original mineral with the gram formula weight and composition represented by the extended formula in table 1. The thermal correction for hygroscopic water (H_2O^- , 0.062 kcal), the correction for bound water (H_2O^+ , 0.034 kcal) as thermally equivalent to ice, the correction for the weight

TABLE 3. - Experimental heats of solution, kcal/mol

SiO ₂ , reaction 1	H ₂ O, reaction 2	MnO, reaction 3	Fe ₂ O ₃ , reaction 4	FeSO ₄ · 7H ₂ O, reaction 5	CaO, reaction 6	H ₂ SO ₄ · 7H ₂ O, reaction 8	$[(Ca_{0.9516})(Mg_{0.0483}$ $Fe^{2+}_{0.7134} Fe^{3+}_{0.0934}$ $Mn_{0.1366})(Si_2O_6)]$, reaction 9
-32.904	+0.822	-47.171	-42.005	-20.649	-55.615	+6.407	-147.656
-32.913	.821	-47.168	-42.029	-20.646	-55.603	6.400	-147.780
-32.916	.821	-47.151	-42.114	-20.645	-55.661	6.467	-147.185
-32.908	.820	-47.129	-42.111	-20.604	-55.634	6.462	-147.624
-32.905	.819	-47.190	-41.944	-20.696	-55.618	6.423	-147.847
	.821	-47.138	-41.936	-20.693		6.430	-147.825
			-42.046	-20.620		6.396	-147.251
			-42.027				
-32.909 ±.005	+0.821 ±.001	-47.158 ±.018	-42.026 ±.047	-20.650 ±.026	-55.626 ±.020	+6.426 ±.022	-147.595 ±.205

percentage of total water, and the net correction for total impurities (0.348 kcal) were made, which gives the corrected heat of solution (-148.270 kcal) for the extended formula weight. This value was then corrected to the adjusted gram formula weight, providing a final value of -148.74 kcal. This final heat of solution value (-148.74±0.40 kcal) contains an allowance for the uncertainties correction procedure.

The final solution after conducting reactions 1 through 7 sequentially in the original charge of acid was identical to the solution obtained after conducting reactions 8 and 9 sequentially in another charge of acid containing an equal amount of K₂Cr₂O₇. The heat of solution values were substituted into the reaction scheme and combined according to

$$\Delta H_{10} = \Delta H_1 + \Delta H_2 + \Delta H_3 + \Delta H_4 + \Delta H_5 + \Delta H_6 + \Delta H_7 - \Delta H_8 - \Delta H_9 = +1.728 \pm 0.401 \text{ kcal,}$$

to obtain the enthalpy change for reaction 10.

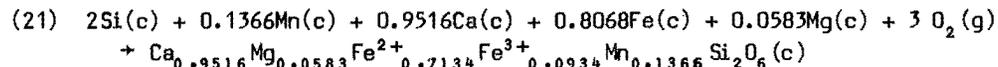
Standard Enthalpy of Formation

The calculation of the standard enthalpy of formation for hedenbergite, requires additional data from the literature. All of the necessary data for the elements and oxides are taken from Pankratz (17), the data for FeSO₄·7H₂O are from DeKock (7), and the data for H₂SO₄·7H₂O are taken from Wagman (25). These values, with their precision uncertainties, are listed in reactions 11 through 20, table 4.

TABLE 4. - Enthalpy of formation of hedenbergite

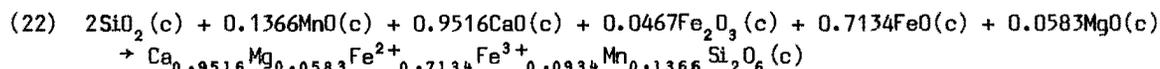
Reaction	ΔH_{298} , kcal/mol	Uncertainty, ±kcal	Refer- ence
(11) Si(c) + O ₂ (g) → SiO ₂ (c).....	-217.720	0.34	17
(12) Mn(c) + 1/2 O ₂ (g) → MnO(c).....	-92.07	.30	17
(13) Ca(c) + 1/2 O ₂ (g) → CaO(c).....	-151.79	.3	17
(14) 2Fe(c) + 1 1/2 O ₂ (g) → Fe ₂ O ₃ (c).....	-197.0	.3	17
(15) Fe(c) + S(rh) + 11/2 O ₂ (g) + 7H ₂ (g) → FeSO ₄ ·7H ₂ O(c).....	-720.44	.14	7
(16) Mg(c) + 1/2 O ₂ (g) → MgO(c).....	-143.76	.1	17
(17) Mg(c) + O ₂ (g) + H ₂ (g) → Mg(OH) ₂ (c).....	-221.100	.2	13
(18) 1/2 O ₂ (g) + H ₂ (g) → H ₂ O(l).....	-68.315	.010	17
(19) S(rh) + 11/2 O ₂ (g) + 8H ₂ (g) → H ₂ SO ₄ ·7H ₂ O(l).....	-687.663	.170	25
(20) Fe(c) + 1/2 O ₂ (g) → FeO(c).....	-65.00	.30	17

$$\Delta H_{21} = \Delta H_{10} + 2\Delta H_{11} + 0.1366\Delta H_{12} + 0.9516\Delta H_{13} + 0.0467\Delta H_{14} + 0.7134\Delta H_{15} + 0.0583\Delta H_{17} + 0.6551\Delta H_{18} - 0.7134\Delta H_{19}$$



$$\Delta H_{21} = -680.960 \pm 0.855 \text{ kcal/mol}$$

$$\Delta H_{22} = \Delta H_{10} + 0.7134\Delta H_{15} + 0.0583\Delta H_{17} - 0.7134\Delta H_{20} - 0.0583\Delta H_{16} + 0.6551\Delta H_{18} - 0.7134\Delta H_{19}$$

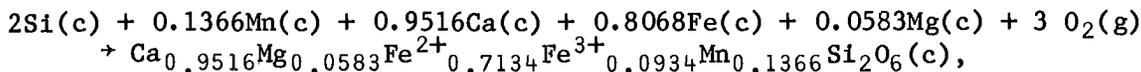


$$\Delta H_{22} = -24.548 \pm 0.485 \text{ kcal/mol}$$

The standard enthalpy of formation for hedenbergite was derived from a selection of these reactions and heats according to the scheme

$$\Delta H_{21} = \Delta H_{10} + 2\Delta H_{11} + 0.1366\Delta H_{12} + 0.9516\Delta H_{13} + 0.0467\Delta H_{14} \\ + 0.7134\Delta H_{15} + 0.0583\Delta H_{17} + 0.6551\Delta H_{18} - 0.7134\Delta H_{19},$$

from which it follows that



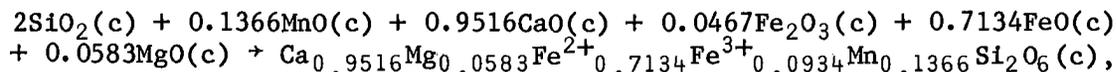
for which

$$\Delta H_{298}^{\circ} = -680.958 \pm 0.855 \text{ kcal/mol.}$$

The enthalpy of formation for hedenbergite from the constituent oxides may be derived by a combination of selected reactions and enthalpy changes, according to the scheme

$$\Delta H_{22} = \Delta H_{10} + 0.7134\Delta H_{15} + 0.0583\Delta H_{17} - 0.7134\Delta H_{20} \\ - 0.0583\Delta H_{16} + 0.6551\Delta H_{18} - 0.7134\Delta H_{19},$$

from which it follows that



for which

$$\Delta H_{298}^{\circ} (\text{from oxides}) = -24.548 \pm 0.485 \text{ kcal/mol.}$$

Low-Temperature Thermal Properties

The heat capacity of hedenbergite was measured by adiabatic calorimetry over the temperature range 12.3 to 300.1 K. Design data and operational details of this calorimeter have been described elsewhere (3, 22).

The hedenbergite sample for low-temperature measurements was dried overnight at 383 K before loading into a 90-mL copper calorimeter vessel. Prior to sealing, the loaded calorimeter vessel was evacuated and backfilled with about 1.9×10^{-3} mol of helium gas to enhance thermal conductivity. A hedenbergite sample of 141.3916 g was used for heat capacity measurements.

The experimental heat capacity values are listed chronologically in table 5 and shown in figure 1. The values for heat capacity and related functions at even temperatures were obtained by computer-smoothing the experimental data, and the resulting values are given in table 6. The heat capacity below 12 K was determined by graphical extrapolation using a C_p/T -versus- T^2 plot. The overall uncertainty of the tabulated smooth heat capacities varied with temperature and was estimated as ± 2 pct for 5 to 15 K, ± 1 pct for 15 to 50 K, ± 0.2 pct for 50 to 200 K, and ± 0.1 pct for 200 to 300 K. Some of the tabulated data are reported to greater resolution only for convenience of rounding.

A second-order transition was observed over the range of approximately 17 to 31 K with a peak temperature of 26.5 K as shown in figure 2. No other transitions were observed.

TABLE 5. - Experimental low-temperature heat capacities of hedenbergite

T, K	Cp°, cal/mol·K	T, K	Cp°, cal/mol·K	T, K	Cp°, cal/mol·K
SERIES I		SERIES IV		SERIES V	
12.33	0.711	25.78	2.989	34.49	3.031
13.64	.835	26.04	3.042	37.59	3.385
15.14	1.004	26.29	3.076	40.93	3.812
16.74	1.210	26.55	3.071	44.56	4.342
18.25	1.449	26.81	3.069	48.52	4.980
19.54	1.662	27.07	3.069	52.83	5.734
20.65	1.872	27.33	3.058	57.55	6.585
21.65	2.087	27.59	3.039	62.73	7.582
22.54	2.291	27.85	2.989	122.79	19.644
23.35	2.460	28.11	2.958	129.52	20.862
24.10	2.646	28.38	2.911	139.39	22.614
24.80	2.810	28.64	2.892	149.18	24.243
SERIES II		28.90	2.871	158.71	25.768
19.02	1.569	29.33	2.823	167.82	27.156
20.21	1.787	29.94	2.792	176.59	28.456
21.24	1.993	30.54	2.771	185.08	29.612
22.16	2.193	31.13	2.771	193.31	30.693
23.00	2.398	31.72	2.796	201.33	31.741
23.78	2.570	32.29	2.809	209.16	32.721
24.50	2.732	32.84	2.890	216.81	33.627
25.18	2.878	33.39	2.925	224.31	34.464
25.82	2.987	46.92	4.713	231.67	35.299
26.19	3.061	50.54	5.330	238.90	36.080
SERIES III		55.09	6.133	245.99	36.821
24.97	2.852	60.02	7.065	253.03	37.492
25.22	2.872	65.44	8.121	259.98	38.180
25.47	2.947	71.38	9.326	266.85	38.830
25.73	2.995	77.92	10.669	273.64	39.474
25.98	3.022	85.13	12.162	280.36	40.027
26.24	3.057	93.06	13.793	287.00	40.598
26.50	3.058	101.80	15.571	293.57	41.153
26.75	3.069	111.16	17.421	300.09	41.630
27.01	3.069	120.75	19.266		
		130.45	21.044		
		140.24	22.762		

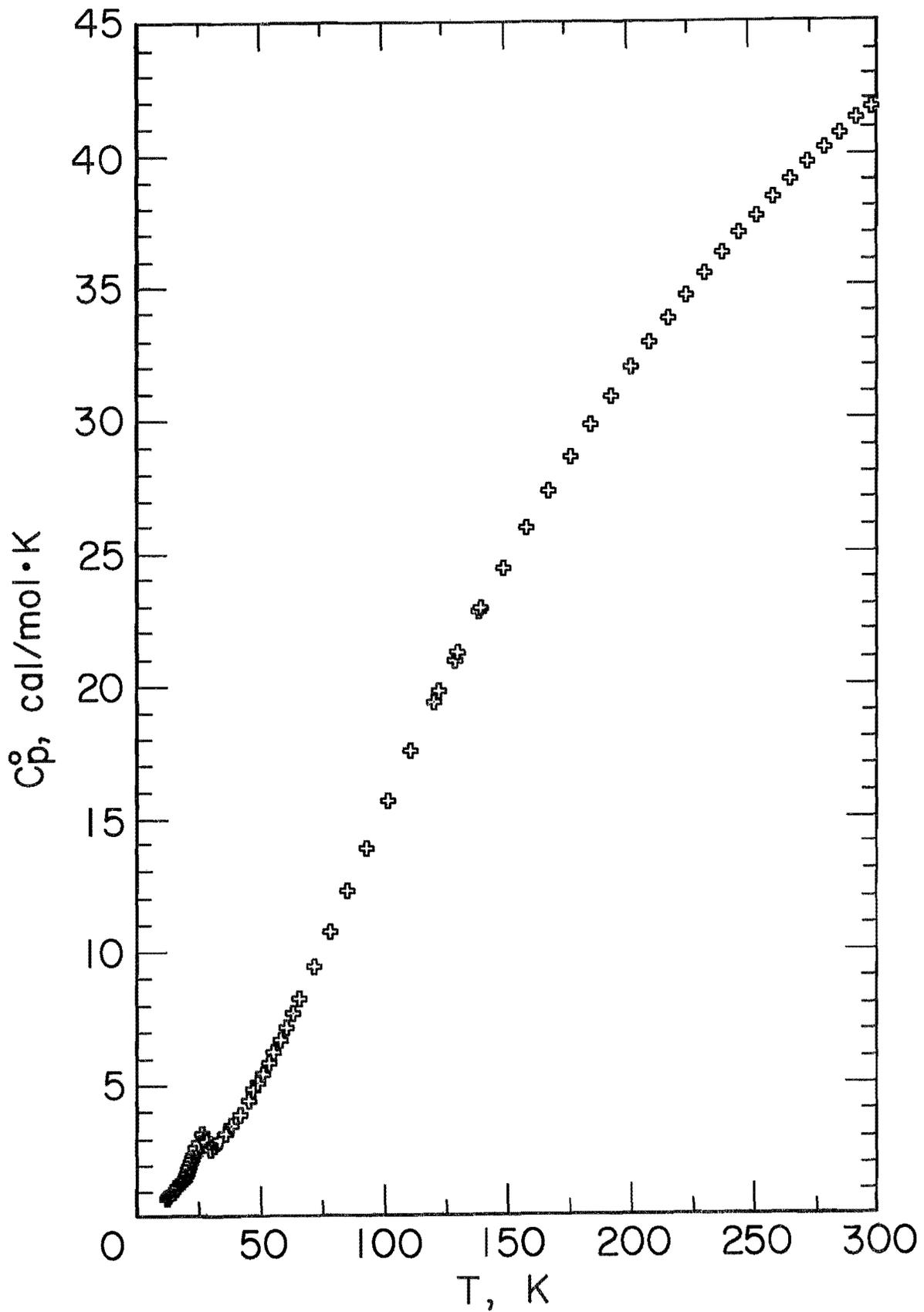


FIGURE 1. - Low-temperature heat capacities of hedenbergite.

TABLE 6. - Thermodynamic functions of hedenbergite

T, K	C_p° , cal/mol·K	$S^\circ(T)-S^\circ(0)$, cal/mol·K	$-[G^\circ(T)-H^\circ(0)]/T$, cal/mol·K	$H^\circ(T)-H^\circ(0)$, kcal/mol
12	0.680	0.504	0.218	0.003
15	.986	.687	.293	.006
20	1.747	1.066	.437	.013
25	2.845	1.571	.611	.024
26	3.029	1.686	.650	.027
¹ 32	2.815	2.289	.904	.044
35	3.080	2.553	1.034	.053
40	3.682	3.002	1.252	.070
45	4.413	3.477	1.472	.090
50	5.231	3.983	1.698	.114
60	7.053	5.095	2.169	.175
70	9.045	6.330	2.674	.256
80	11.103	7.672	3.214	.357
90	13.167	9.099	3.788	.478
100	15.206	10.592	4.393	.620
110	17.195	12.135	5.027	.782
120	19.117	13.714	5.685	.964
130	20.961	15.318	6.364	1.164
140	22.720	16.936	7.061	1.382
150	24.394	18.561	7.773	1.618
160	25.983	20.186	8.499	1.870
170	27.490	21.807	9.234	2.137
180	28.920	23.419	9.977	2.420
190	30.280	25.020	10.727	2.716
200	31.573	26.606	11.481	3.025
210	32.807	28.177	12.239	3.347
220	33.984	29.730	12.999	3.681
230	35.110	31.266	13.760	4.027
240	36.186	32.783	14.521	4.383
250	37.214	34.281	15.281	4.750
260	38.196	35.760	16.040	5.127
270	39.129	37.219	16.798	5.514
273.15	39.413	37.675	17.036	5.637
280	40.014	38.658	17.553	5.909
290	40.848	40.077	18.305	6.314
298.15	41.491	41.218	18.916	6.649
300	41.690	41.475	19.054	6.726
400	47.619	54.315	26.306	11.203
500	52.046	65.447	33.046	16.201
600	54.814	75.205	39.277	21.557
700	56.284	83.778	45.035	27.120
800	56.999	91.346	50.360	32.788
900	57.423	98.085	55.295	38.511
1,000	57.801	104.155	59.883	44.272
1,100	58.152	109.681	64.163	50.070
1,200	58.375	114.751	68.170	55.898

¹2d-order transition.

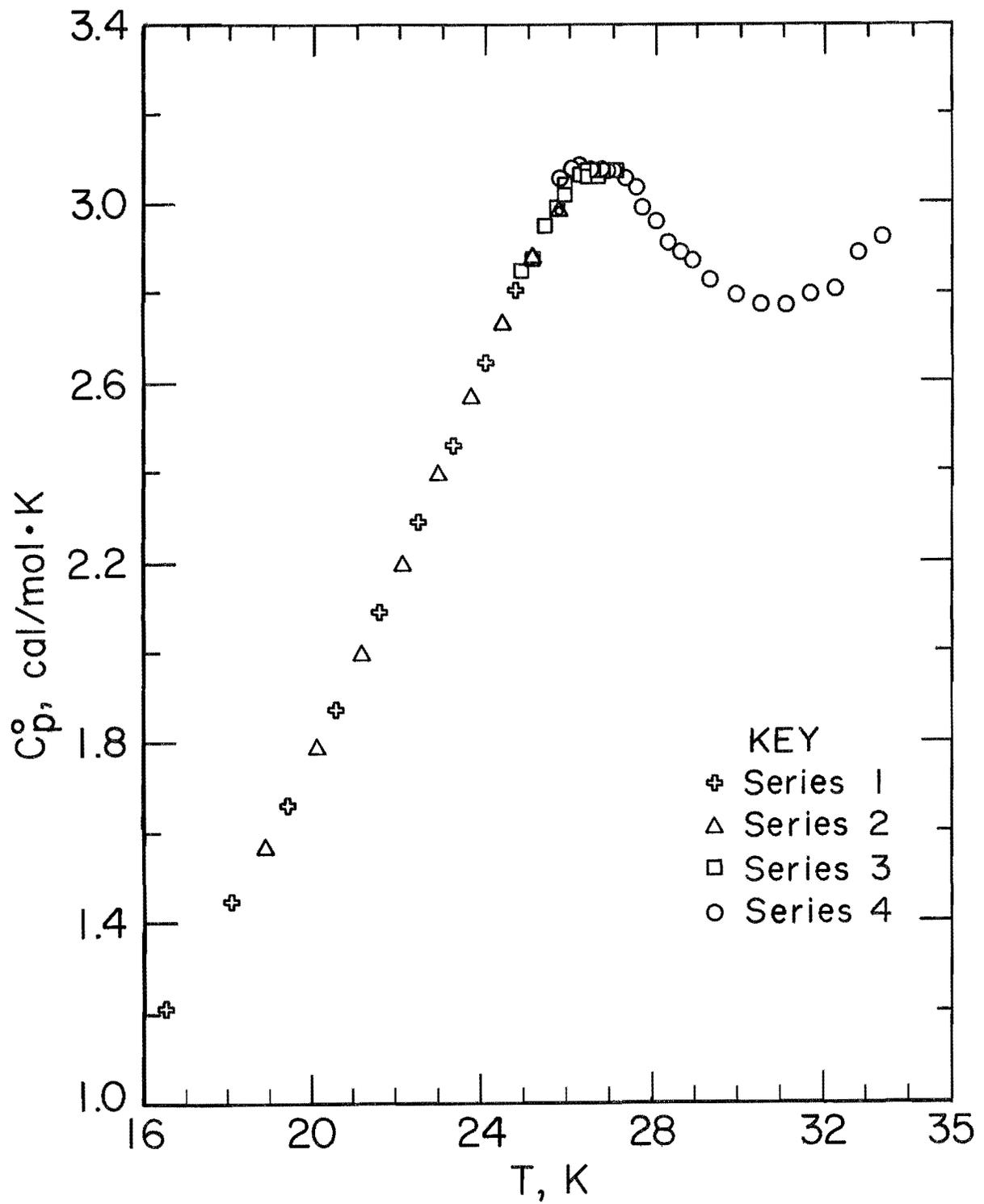


FIGURE 2. - Heat capacities of hedenbergite in the transition region.

High-Temperature Thermal Determinations

The heat capacity of hedenbergite was measured with a differential scanning calorimeter (DSC) over the temperature range 397 to 1,147 K. The DSC was a model TA2000C manufactured by the Mettler Corp. and has a nominal operating range of 298 to 1,473 K.

A 0.10726-g sample of hedenbergite was loaded into a 0.47047-g platinum capsule, and both the full capsule and an empty reference capsule were placed in the DSC. The DSC chamber was evacuated and filled with argon, and operated at a scan rate of 10 K/min in 50-K steps from 322 to 1,172 K. The heat capacity measurements were discontinued above 1,173 K in order to avoid decomposition to CaSiO_3 , tridymite, and olivine as reported by Bowen (4). The collected data were analyzed according to the "enthalpy method," as described by Mraw (15). The accuracy of the DSC was determined by measuring the heat capacity of MgO and comparing the measured values to accepted values from Pankratz (17). The uncertainties of the heat capacities are ± 3 pct from 298 to 700 K and ± 2 pct from 700 to 1,473 K.

The experimental heat capacities, shown in table 7 and figure 3, were fit to a polynomial by least squares and joined smoothly to the low-temperature values. The smooth values along with the related functions are shown in table 6.

Thermodynamic Properties of Hedenbergite

The experimentally determined thermal data for hedenbergite, the enthalpy of formation, low-temperature heat capacity, and high-temperature thermal data, may be combined with the necessary data for the constituent elements and oxides for the calculation of the enthalpies, Gibbs energies of formation, and other relevant properties as a function of temperature. The thermodynamic properties for the formation of hedenbergite from the elements and oxides are presented in tables 8 and 9, respectively. Hedenbergite is shown to be stable throughout the range of the data.

DISCUSSION

The mineral hedenbergite is closely similar to iron-refining slags in both structure and composition. The specimen used in this study shows the characteristic presence of manganese but with a fairly low concentration of magnesium. An excellent review is presented by Deer (6).

There were no experimentally determined thermodynamic data for hedenbergite found in the literature; values from other experimental work have been calculated,

TABLE 7. - Experimental high-temperature heat capacities of hedenbergite

T, K	C_p° , cal/mol·K	T, K	C_p° , cal/mol·K	T, K	C_p° , cal/mol·K
397	46.36	697	56.38	997	58.10
447	51.00	747	56.66	1,047	57.33
497	52.09	797	55.78	1,097	57.96
547	53.40	847	57.12	1,147	58.11
597	54.64	897	58.20		
647	55.84	947	58.29		

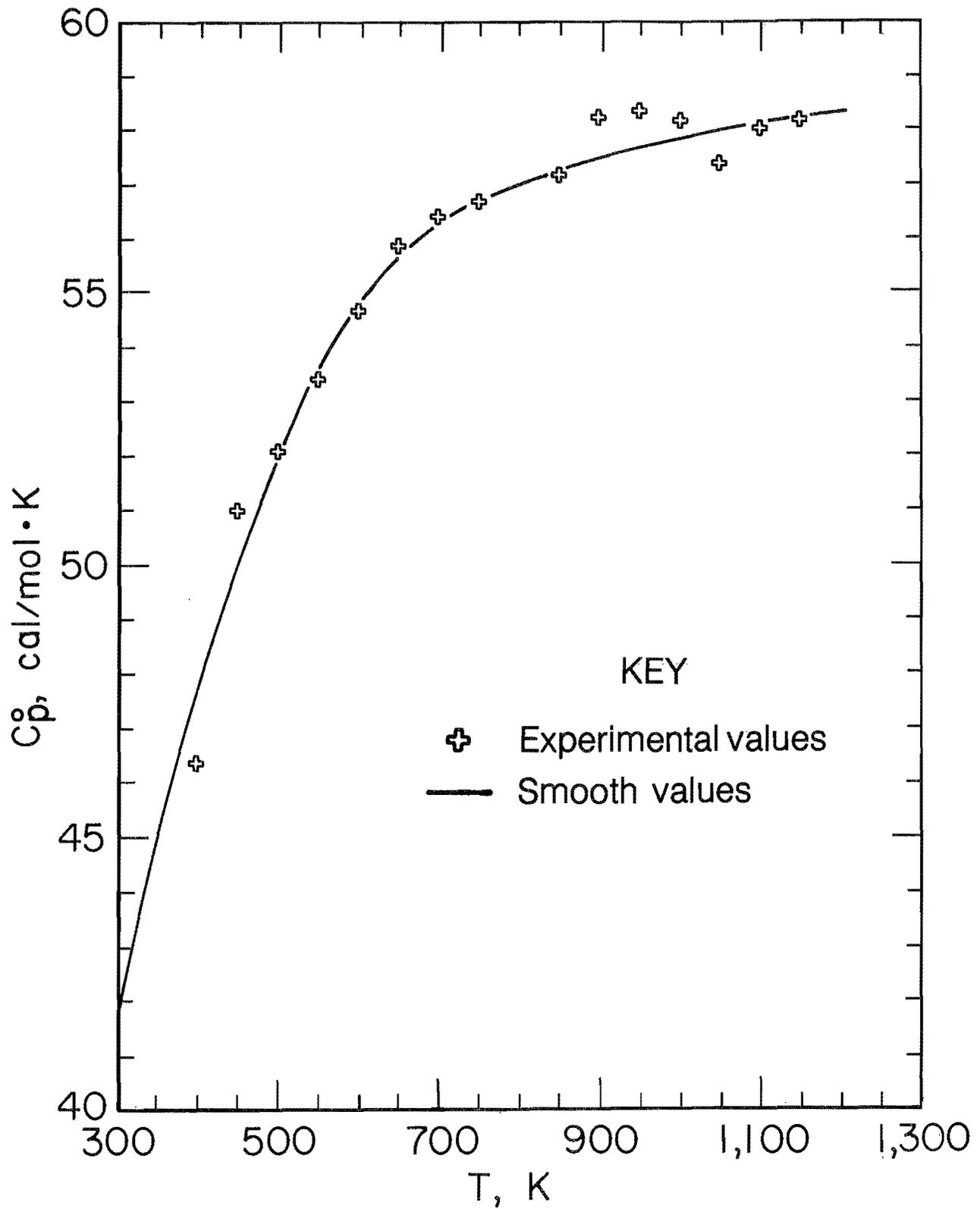


FIGURE 3. - High-temperature heat capacities of hedenbergite. The smooth values join the low-temperature values at 300 K.

TABLE 8. - Standard formation data for hedenbergite, reaction
 $[0.9516\text{Ca}(c,\ell,g) + 0.0583\text{Mg}(c,\ell,g) + 0.8068\text{Fe}(c,\ell) + 0.1366\text{Mn}(c,\ell)$
 $+ 2\text{Si}(c,\ell) + 3\text{O}_2(g) = \text{Ca}_{0.9516}\text{Mg}_{0.0583}\text{Fe}_{0.8068}\text{Mn}_{0.1366}\text{Si}_2\text{O}_6](c)$

T, K	cal/mol·K			kcal/mol			Log Kf
	Cp°	S°	-(G° - H° ₂₉₈)/T	H° - H° ₂₉₈	ΔHf°	ΔGf°	
298.15	41.491	41.218	41.218	0	-680.960	-641.897	470.517
300	41.690	41.475	41.218	.077	-680.962	-641.653	467.438
400	47.619	54.315	42.930	4.554	-680.844	-628.564	343.427
500	52.046	65.447	46.343	9.552	-680.426	-615.534	269.046
600	54.814	75.205	50.358	14.908	-679.865	-602.607	219.497
700	56.284	83.778	54.534	20.471	-679.303	-589.782	184.136
¹ 720	56.427	85.366	55.368	21.598	-679.202	-587.223	178.244
720	56.427	85.366	55.368	21.598	-679.411	-587.220	178.243
800	56.999	91.346	58.672	26.139	-679.010	-576.999	157.627
900	57.423	98.085	62.683	31.862	-678.676	-564.253	137.018
² 922	57.506	99.473	63.544	33.126	-678.639	-561.457	133.085
922	57.506	99.473	63.544	33.126	-678.764	-561.457	133.085
³ 980	57.725	102.988	65.776	36.468	-678.741	-554.080	123.564
980	57.725	102.988	65.776	36.468	-678.814	-554.080	123.564
1000	57.801	104.155	66.532	37.623	-678.834	-551.535	120.536
⁴ 1,043	57.952	106.592	68.134	40.112	-678.962	-546.059	114.420
1,100	58.152	109.681	70.207	43.421	-679.049	-538.804	107.049
⁵ 1,112	58.179	110.312	70.637	44.119	-679.060	-537.282	105.595
1,112	58.179	110.312	70.637	44.119	-681.001	-537.276	105.594
⁶ 1,185	58.342	114.017	73.195	48.374	-680.763	-527.852	97.351
1,185	58.342	114.017	73.195	48.374	-680.936	-527.852	97.351
1,200	58.375	114.751	73.710	49.249	-680.863	-525.916	95.781

¹α-β transition of Ca.

³α-β transition of Mn.

⁵Melting point of Ca.

²Melting point of Mg.

⁴Curie temperature of Fe.

⁶α-γ transition of Fe.

TABLE 9. - Formation data for hedenbergite from the oxides, reaction
 $[2\text{SiO}_2(\text{qtz}) + 0.1366\text{MnO}(\text{c}) + 0.9516\text{CaO}(\text{c}) + 0.0467\text{Fe}_2\text{O}_3(\text{c})$
 $+ 0.7134\text{FeO}(\text{c}) + 0.0583\text{MgO}(\text{c})$
 $= \text{Ca}_{0.9516}\text{Mg}_{0.0583}\text{Fe}^{2+}_{0.7134}\text{Fe}^{3+}_{0.0934}\text{Mn}_{0.1366}\text{Si}_2\text{O}_6(\text{c})]$

T, K	cal/mol·K			kcal/mol			Log Kf
	Cp°	S°	-(G° - H° ₂₉₈)/T	H° - H° ₂₉₈	ΔH°	ΔG°	
298.15	41.491	41.218	41.218	0	-24.548	-24.220	17.753
300	41.690	41.475	41.218	.077	-24.550	-24.219	17.643
400	47.619	54.315	42.930	4.554	-24.644	-24.095	13.165
500	52.046	65.447	46.343	9.552	-24.701	-23.948	10.468
600	54.814	75.205	50.358	14.908	-24.747	-23.793	8.667
700	56.284	83.778	54.534	20.471	-24.866	-23.627	7.377
800	56.999	91.346	58.672	26.139	-25.169	-23.432	6.401
¹ 847	57.198	94.606	60.577	28.823	-25.505	-23.318	6.017
847	57.198	94.606	60.577	28.823	-25.855	-23.317	6.016
900	57.423	98.085	62.683	31.862	-25.970	-23.156	5.623
² 960	57.650	101.799	65.013	35.314	-26.116	-22.963	5.227
960	57.650	101.799	65.013	35.314	-26.116	-22.963	5.227
1,000	57.801	104.155	66.532	37.623	-26.196	-22.829	4.989
1,100	58.152	109.681	70.207	43.421	-26.403	-22.485	4.467
1,200	58.375	114.751	73.710	49.249	-26.624	-22.118	4.028

¹α-β transition of SiO₂.

²Curie temperature of Fe₂O₃.

however. Taylor and Liou (23) present an entropy value ($S_{298}^{\circ} = 40.1$ cal/mol·K) and a mean standard enthalpy of formation value ($\Delta H_{298}^{\circ} = -678.15$ kcal/mol). Yakovlev (26) also presents a calculated enthalpy value ($\Delta H_{298}^{\circ} = -677.508$ kcal/mol). Navrotsky (16) calculated a standard Gibbs energy of formation value ($\Delta G^{\circ} = -25.8 \pm 1.5$ kcal/mol) from high-temperature data on the oxide components. All of these calculated values pertain to the ideal formula ($\text{CaFeSi}_2\text{O}_6$) and are in substantial agreement with the results reported here.

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